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(54) Method of coating inorganic particles

(57) A single-stage method of providing inorganic particles with a polymeric organic coating comprises contacting inorganic particles with an organic compound in the presence of a corona discharge which is produced in a gaseous medium between two electrodes at least one of which is electrically insulated from the medium. The organic compound is caused to polymerise by the corona discharge and a polymer coating is formed on the inorganic particles.

Many types of inorganic particles can be coated such as pigments, fillers and extenders and inorganic borides, carbides and nitrides. The organic polymeric coating helps to improve the compatibility of pigments or fillers with organic media and tends to reduce the rate of hydrolysis of solids such as aluminium nitride.

The organic compound is, for example, a saturated or unsaturated hydrocarbon, a halogenated or an acrylic compound. In the examples titanium dioxide or aluminium nitride is coated with polyethylene. The gaseous medium is preferably an inert gas. In an apparatus for carrying out the process one electrode may comprise a cylinder and the other electrode is positioned within the cylinder along the axis thereof, and the barrier of insulating material is quartz or glass.

FORMAL SPECIFICATION

COATING PROCESS

This invention relates to a coating process and in particular to a method of coating inorganic particles with a polymeric organic material.

Coated particles of inorganic compounds are well known especially where the particles are used as pigments, fillers and extenders in systems such as paints, inks and plastics, since the coatings on the particles have been shown to improve the physical properties of the inorganic compounds. It is particularly desirable that pigment or filler particles should be readily dispersible in organic media in order to maximise their efficiency as additives. An organic coating on the inorganic particles renders them more compatible with organic media and hence more easily dispersed.

It is an object of this invention to provide a simple, single-stage method of providing inorganic particles with a polymeric organic coating.

According to the invention a process for coating inorganic particles with a polymeric organic material comprises contacting the particles with an organic compound in the presence of a corona discharge, the said corona discharge being produced by capacitively exciting a gaseous medium lying between two spaced electrodes at least one of which is electrically insulated from the gaseous medium by a barrier of electrically insulating material and said organic compound being a compound which is polymerised by the influence of said corona discharge.

According to a preferred embodiment of the invention the inorganic particles are suspended in a mixture of an inert ionisable gas and the organic compound and the suspension thus produced is caused to flow between the spaced electrodes whilst a corona discharge is maintained in the region between the electrodes.

The process of the invention is suitable for coating a wide range of inorganic particulate materials. Typically it is used for coating those inorganic particles which are used as fillers, pigments and extenders in organic media. Particularly, the process is of use for inorganic pigments such as titanium dioxide pigments, aluminium oxide pigments, antimony oxides, barium pigments, calcium pigments, zirconium pigments, chromium pigments and magnesium pigments. Extenders and/or fillers such as carbonates, silica, silicates, aluminates and clays can be coated by the process of the invention as can be mixtures of pigments and extenders or fillers. Non-pigmentary forms of those inorganic compounds mentioned as pigments are also suitable for the process. The process is also useful for coating inorganic nitrides, borides and carbides such as titanium nitride, aluminium nitride, boron nitride, titanium boride, silicon carbide and titanium carbide. In the most preferred process the inorganic particles are particles of titanium dioxide pigment, preferably rutile titanium dioxide.

The process can be operated with a very wide range of particle sizes for example from 0.01 micron to about 1 mm but the inorganic particles preferably have an average size of from 0.01 micron to 100

microns and more preferably from 0.1 micron to 5 microns. When the inorganic particles are of titanium dioxide pigment their average particle size is preferably from 0.1 micron to 0.4 micron. Desirably the inorganic particles are in a finely divided state prior to coating and, if necessary, can be milled by any suitable means to achieve such a state.

Any organic compound which is polymerised by the influence of the corona discharge can be used in the process of the invention. Even many organic compounds not generally polymerisable by chemical techniques can be used. Preferably the organic compound is present in the process in the form of a gas or vapour and particularly suitable compounds are saturated and unsaturated aliphatic hydrocarbons such as methane, ethane, ethylene, butadiene and acetylene, aromatic hydrocarbons such as benzene, toluene and styrene, halogenated hydrocarbons such as chloroform, tetrafluoroethylene, carbon tetrachloride and tetrafluoromethane and acrylic compounds such as acrylonitrile, acrylic acid, methacrylic acid and acrylic or methacrylic esters.

The corona discharge is produced by capacitively exciting a gaseous medium. This medium can be any medium which is ionised by the corona discharge but, typically it consists of an inert gas such as argon, helium or nitrogen.

A feature of the gaseous medium when subjected to the corona discharge is that the electrons produced by ionisation possess relatively high energies by comparison with the molecules of the

medium. Typically the electrons have an average energy greater than 0.16 eV and the molecules have an average energy less than 0.08 eV.

The corona discharge is produced between two spaced electrodes at least one of which is insulated from the gaseous medium. Typically a glass or quartz barrier is provided between the electrodes and the gaseous medium. In a particularly suitable arrangement of electrodes one electrode is positioned axially within a glass or quartz tube and the other electrode consists of a cylinder within which the glass or quartz tube and axial electrode are located. The axial electrode may also be insulated from the gaseous medium by a glass or quartz sheath. When both electrodes are insulated from the gaseous medium the discharge is termed electrodeless discharge but where a single barrier is employed the phenomenon is termed a semicorona discharge. Both terms are intended to be covered by the general description "corona discharge" used herein.

A corona discharge is capacitive and limited in origin to alternating currents. It is characterised by high voltage and low current. A range of frequencies from about 1 KHz to about 100 MHz can be used but frequencies of from about 100 KHz to about 20 MHz are preferred.

The current, voltage and power used to generate the corona discharge is governed to some extent by the construction of the apparatus used but with two quartz barriers of 1.5 mm thickness separated by about 12 mm spacing a voltage of between 5 and 10 KV

has been found suitable. The energy input is usually sufficient to produce at least 0.25 GJ/kg of the organic compound used.

A corona discharge may be maintained over a wide range of pressure conditions. Typically pressures of from 20 kPa to 1 MPa are used but a preferred pressure is from 80 to 120 kPa. A particular advantage of the method of this invention is the fact that it can be operated at approximately atmospheric pressure (100 kPa).

The inorganic particles may be brought into contact with the organic compound in any suitable manner provided that there is contact in the presence of the corona discharge. For example, when an ionisable inert gas is passed between a pair of electrodes which are arranged to produce a corona discharge there is produced on the downstream side of the electrodes a region known as the afterglow region. The inorganic particles can be introduced separately or in admixture with the organic compound into this afterglow region to produce a polymeric coating. Alternatively, the organic compound can be passed between the electrodes together with the ionisable inert gas and the inorganic particles introduced into the afterglow region.

The inorganic particles can be coated with the organic compound prior to the coated inorganic particles being subjected to the effect of the corona discharge.

In a particularly preferred embodiment the inorganic particles, an inert ionisable gas and the organic compound are passed between the electrodes in such a manner that the inorganic particles remain

suspended in the gaseous medium whilst a corona discharge is maintained between the electrodes.

In this preferred embodiment the proportion of organic compound in the inert gas is preferably maintained between 1% and 10% by volume and the weight ratio of inorganic particles to organic compound is preferably from 30:1 to 1:2 by weight.

The process of the invention provides a simple method of coating inorganic particles without involving the use of reagents other than the inorganic particles and the organic compound. It avoids the steps of separation and drying which are associated with coating by polymerisation in organic or aqueous media.

The products of the process are evenly coated with a polymeric layer derived from the organic compound. This layer assists in preventing agglomeration of particles on storage and aids in dispersing the particles in organic media by rendering them more compatible with the media.

The coating also reduces the rate of hydrolysis of powders such as aluminium nitride which react with atmospheric moisture.

The invention is particularly described by the following examples.

Example 1

A coating reactor was constructed from a 300 mm length of 30 mm diameter silica tubing. An cylindrical electrode of length 60 mm was positioned outside the tube and coaxial with it. A rod electrode was positioned along the axis of the tube within the cylindrical

electrode. This second electrode was insulated from the contents of the reactor by a quartz tube with a diameter of 8 mm. The assembly of reactor and electrodes was positioned with the axis of the reactor vertical.

Argon was introduced into the space between the electrodes at atmospheric pressure and a flow rate of approximately 1 l/min. A radio frequency power supply (EN1 Power Systems Model HPG-2) was connected to the two electrodes and adjusted to supply power at a rate of 50 watts. The frequency of the power supply was then increased until a corona discharge was observed between the electrodes at a frequency of about 275 KHz.

Ethylene was then introduced into the space between the electrodes at a flow rate of approximately 0.03 l/min and the power supplied to the electrodes was increased to 75 watts.

Titanium dioxide powder which had previously been dried at 300°C was then dropped into the space between the electrodes at a rate of 1 g/min.

The coated titanium dioxide was collected in a trap positioned below the reactor and examined by electron microscopy. A uniform coating of polyethylene approximately 5 nm thick was observed on the titanium dioxide particles.

Example 2

The reactor of Example 1 was modified by fitting a powder inlet to the quartz tube so as to allow powder to be dropped into the afterglow region of the corona discharge when the reactor was

positioned horizontally. A collection vessel was fitted to the reactor diametrically opposite the powder inlet.

The reactor assembly was positioned horizontally and argon was introduced into the space between the electrodes at a rate of approximately 1 l/min at atmospheric pressure. A radio frequency power supply was connected to the electrodes and adjusted as in Example 1 to produce a corona discharge at a power of 50 watts.

Ethylene was introduced into the space between the electrodes at a flow rate of approximately 0.03 l/min and the power was adjusted to 75 watts.

Dried titanium dioxide was then dropped through the powder inlet at a rate of 0.5 g/min and collected in the collection vessel.

Examination by electron microscopy showed that the particles of titanium dioxide had been coated with a layer of polyethylene with a thickness varying up to about 60 nm.

Example 3

Example 1 was repeated except that aluminium nitride which had been dried at 300°C was used in place of the titanium dioxide. The aluminium nitride was added at a rate of 0.5 g/min.

Samples of treated aluminium nitride and untreated aluminium nitride were suspended in water at a concentration of 100 g/l and the pH of the suspension was monitored. Initially the pH of the suspension of untreated aluminium nitride was 6.1 and it rose to 8.0 after 1 hour whereas the pH of the suspension of treated aluminium nitride rose from an initial value of 5.4 to 6.5 after 1 hour.

CLAIMS

1. A process for coating inorganic particles with a polymeric organic material comprising contacting the particles with an organic compound in the presence of a corona discharge, said corona discharge being produced by capacitively exciting a gaseous medium lying between two spaced electrodes at least one of which is electrically insulated from the gaseous medium by a barrier of electrically insulating material and said organic compound being a compound which is polymerised by the influence of said corona discharge.

2. A process according to claim 1 in which the inorganic particles are suspended in a mixture of the organic compound and an inert ionisable gas and the suspension thus produced is caused to flow between the spaced electrodes whilst a corona discharge is maintained in the region between the electrodes.

3. A process according to claim 1 or 2 in which the inorganic particles are particles of a filler, pigment or extender.

4. A process according to claim 3 in which the pigment is titanium dioxide pigment.

5. A process according to claim 1 or 2 in which the inorganic particles are particles of an inorganic nitride, boride or carbide.

6. A process according to any one of the preceding claims in which inorganic particles have a particle size of from 0.01 micron to 1 millimeter.

7. A process according to any one of claims 1 to 5 in which the inorganic particles have an average particle size of from 0.01 micron to 100 microns.

8. A process according to claim 7 in which the average particle size is from 0.1 micron to 5 microns.

9. A process according to claim 4 in which the particles have an average particle size of from 0.1 micron to 0.4 micron.

10. A process according to any one of the preceding claims in which the inorganic particles are milled prior to contact with the organic compound.

11. A process according to any one of the preceding claims in which the organic compound is present in the form of a gas or vapour.

12. A process according to any one of the preceding claims in which the organic compound is a saturated or unsaturated aliphatic hydrocarbon, an aromatic hydrocarbon, a halogenated hydrocarbon or an acrylic compound.

13. A process according to any one of the preceding claims in which the gaseous medium comprises an inert gas.

14. A process according to any one of the preceding claims in which the electrons produced by ionisation of the gaseous medium in the corona discharge possess an average energy greater than 0.16 eV.

15. A process according to any one of the preceding claims in which the corona discharge is generated at a frequency of from about 1 KHz to about 100 MHz.

16. A process according to claim 15 in which the frequency is from about 100 KHz to about 20 MHz.

17. A process according to any one of the preceding claims in which an amount of energy equivalent to at least 0.25 GJ/kg of organic compound used is supplied.

18. A process according to any one of the preceding claims in which the gaseous medium is maintained at a pressure of from 20 kPa to 1 MPa.

19. A process according to claim 18 in which the pressure of the gaseous medium is from 80 kPa to 120 kPa.

20. A process according to claim 19 in which the pressure is approximately 100 kPa.

21. A process according to claim 1 in which an inert ionisable gas is caused to flow between a pair of electrodes whilst a corona discharge is generated within said gas and the inorganic particles are contacted with the organic compound in the afterglow region which forms on the downstream side of the electrodes.

22. A process according to claim 1 in which the inorganic particles are coated with the organic compound prior to the coated particles so formed being subjected to the effect of the corona discharge.

23. A process according to claim 2 in which the proportion of organic compound in the inert gas is from 1% to 10% by volume.

24. A process according to claim 2 or 23 in which the weight ratio of inorganic particles to organic compound is from 30:1 to 1:2 by weight.

25. An apparatus for carrying out the process of any one of the preceding claims in which one electrode comprises a cylinder and the other electrode is positioned within this cylinder and along the axis thereof.

26. An apparatus according to claim 25 in which the barrier of electrically insulating material is glass or quartz.

27. A process for coating inorganic particles substantially as described herein with reference to the Examples.

Amendments to the claims have been filed as follows

25. A process according to any one of the preceding claims in which one of the two spaced electrodes comprises a cylinder and the other spaced electrode is positioned within this cylinder and along the axis thereof.

26. A process according to any one of the preceding claims in which the barrier of electrically insulating material is glass or quartz.

Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

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(ii) Int Cl (Edition 5) C08F; C08G

Search Examiner

B J BALDOCK

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES : DERWENT WPI, WPIL

Date of Search

2 MARCH 1992

Documents considered relevant following a search in respect of claims 1 TO 24 AND 27

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1342748 EASTMAN KODAK see Claims 1 to 3, 6, 7, Examples 1, 2, page 2 line 52 to page 3 line 40, page 3 lines 51-70, page 5 lines 70-95	At leas 1,3,6,7 11,12
A	US 4869922 AUSIMONT see Claim 1, Examples 1,4,5, figure 1	At leas 1
X	US 4810524 TDK CORP see figure 1, Example 1, Claims 1 to 8, column 2 line 45 to column 4 line 45	1,2,3, 11 to 1
X	JP 060047004 A SHINGIJUTSU see WPI Accession No: 85-102022/17	At leas 1
X	JP 074040791 B NITTO ELEC see WPI Accession No: 74-83694V/48	1,3,11, 12

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to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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